The invention relates to perfluorodiacylperoxides used as polymerization initiators in a wide temperature range.

Specifically the invention relates to perfluorodiacylpe-roxides obtainable with good yields from the respective per-fluoroacylfluorides and having a high hydrolytic stability, in particular when used as polymerization initiators in aqueous medium. The high hydrolytic stability of said initiators confers to the polymerization process improved yields while the perfluorinated structure of the initiator allows to obtain polymers having stable perfluoroalkyl end groups.

The use as polymerization initiators of halogenated diacylperoxides is known in the prior art. These compounds can be obtained by synthesis from the respective acyl-halides, using various methods described in the literature. The per-fluorodiacylperoxide synthesis from the respective perfluoro-acyl-halides in the presence of H_2O_2 and NaOH is described, for example, by H. Sawada in Chemical Review, 1996, Vol.96, 1779-1808. In the prior art to synthesize perfluorodiacylperoxides, perfluoroacylchlorides are preferably used since they are more reactive than the corresponding perfluoroacylfluorides. In

fact, perfluoroacylfluorides determine lower synthesis yie-
lds than the corresponding chlorides. Besides, the obtained
perfluorodiacylperoxides cause secondary reactions since they
are easily hydrolyzed by the reaction medium wherein they are
produced.

The perfluorodiacylperoxides exemplified in the prior art
as polymerization initiators give low yields when used in
polymerization processes in aqueous medium. To overcome this
drawback one can polymerize in the presence of solvent.
However the polymerization in solvent is more expensive than
that in aqueous medium. Besides, it is necessary to use
particular solvents which have no environmental impact,
otherwise supplementary units would be necessary for their
treatment. Besides, the polymerization in aqueous medium
allows to generally obtain higher polymerization yields and a
better control of the molecular weights of the polymers.

From the industrial point of view it is therefore advan-
tageous to polymerize in aqueous medium using initiators which
are not hydrolyzed in the reaction medium. On the other hand
non fluorinated initiators are known, for example ammonium
persulphate, which have a good hydrolytic stability, thus
allowing the water polymerization with good yields. However
these initiators have the drawback to lead to the obtainment
of polymers having unstable end groups and therefore unusable

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in applications where a high stability and a high purity degree of the final polymer are required, for example in optical applications. For these uses it would be necessary to treat them to obtain stable end groups.

In GB 781,532 it is described the polymerization of perfluoro-olefins using perfluorinated or chlorofluorinated solvents in the presence of initiators. In said patent it is pointed out how the use of perfluorinated peroxides as polymerization initiators in aqueous medium is not possible since the presence of water determines the deactivation of the peroxide itself already at temperatures higher than 0°C.

USP 3,671,510 points out how the perfluorodiacylperoxides are hydrolyzed in the presence of water, wherefore the initiator efficiency is strongly compromised and therefore the monomer conversion is notably reduced. To overcome these inconveniences, this patent suggests the use of (perchloro-fluoro)-di-acylperoxides as polymerization initiators in aqueous medium. However, the use of said peroxides implies the drawback to give polymers having unstable end groups with the above disadvantages.

EP 606,492 refers to a polymerization process in aqueous phase of tetrafluoroethylene with hexafluoropropene, wherein difluoroacylperoxides are used as polymerization initiators in the presence of suitable perfluoroalkylcarboxylic acids. Said
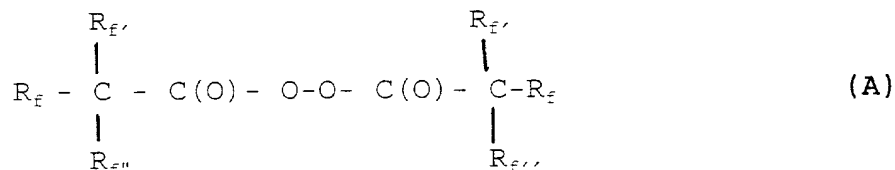
perfluoroalkylcarboxylic acids decrease the tendency to hydro-
lysis of perfluoroacylperoxides. However, by operating in acid
medium there is the drawback to have a poor stability of the
obtained polymer latex.

The easiness to hydrolysis of perfluorodiacylperoxides is
more stressed for the compounds having a low molecular weight,
see Sawada et al in Chem. Abs. Vol. 112:117996b and patent
application WO 97/08142. Said patent application describes a
synthesis method to limit the tendency to hydrolysis of the
obtained perfluorodiacylperoxides. The process variables, for
example reaction temperature, contact time among reactants,
mixing and ratio among reactants, must be very carefully
determined and strictly maintained constant during the
process. To maintain these variables in the narrow range
useful to avoid hydrolysis, one uses complicated equipments,
as ultrasound systems or micro-ejectors. The drawback of the
described process resides in that it is difficult to bring it
on an industrial scale.

The Applicant has surprisingly found perfluorodiacylpero-
xides having end groups with branched or cyclic structure,
which are not hydrolyzed in aqueous medium for long times at
the corresponding temperatures of thermal decomposition.
Depending on their decomposition temperature they are usable
as polymerization initiators in a wide temperature range, from

-20°C to 100°C, and they allow to obtain improved yields (see the comparative Examples).
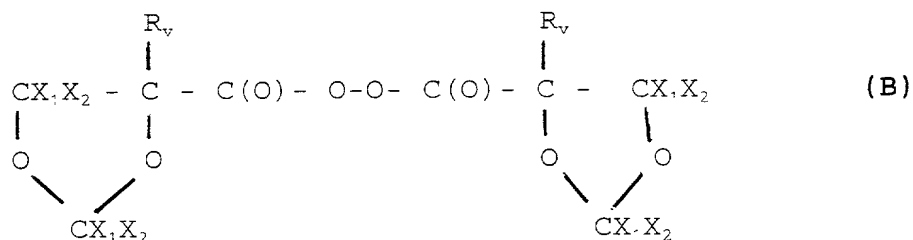
An object of the present invention are therefore perfluorodiacylperoxides having the following structures:

$$R_f - \underset{\underset{R_{f''}}{|}}{\overset{\overset{R_{f'}}{|}}{C}} - C(O) - O-O- C(O) - \underset{\underset{R_{f''}}{|}}{\overset{\overset{R_{f'}}{|}}{C}} - R_f \qquad \textbf{(A)}$$

wherein:

when R_f is F, $R_{f'}$, $R_{f''}$ are both $-CF_3$;

when R_f is $-CF_3$, $R_{f'}$, $R_{f''}$ are C_1-C_3 linear or branched perfluorooxyalkyl groups;

$$CX_1X_2 - \underset{\underset{O}{|}}{\overset{\overset{R_v}{|}}{C}} - C(O) - O-O- C(O) - \underset{\underset{O}{|}}{\overset{\overset{R_v}{|}}{C}} - \underset{\underset{O}{\backslash}}{CX_1X_2} \qquad \textbf{(B)}$$

$$CX_1X_2 \qquad\qquad\qquad CX_1X_2$$

wherein:

R_v is selected from F, perfluorooxyalkyl, C_1-C_3 linear or branched perfluoroalkyl;

X_1, X_2 are selected from F, perfluoroalkyl, C_1-C_3 linear or branched perfluorooxyalkyl.

$$CF_2 \overline{\qquad} CX_3 - C(O) - O-O- C(O) - CX_3 \overline{\qquad} CF_2 \qquad \textbf{(C)}$$

$$(CF_2)_n \overline{\qquad} CF_2 \qquad\qquad\qquad (CF_2)_n \overline{\qquad} CF_2$$

wherein:

n = 1-3

X_3 is selected from F, C_1-C_3 linear or branched perfluoro-

alkyl, with the proviso that for n = 3, X_3 cannot be F;

said perfluorodiacylperoxides meet the following condition:

the thermal decomposition constants K_d (sec^{-1}) in the presence

of water do not undergo substantial variations with respect to

the thermal decomposition constants in absence of water.

This means that the perfluorodiacylperoxides of the

invention can be used as initiators in aqueous polymerization

without any variation of the half-life times determined under

anhydrous conditions. Therefore the invention compounds can be

used also after storage in aqueous emulsion for long times,

even over 2-3 days, without undergoing any hydrolytic

decomposition. This represents a further advantage from the

industrial point of view since there is no need of immediate

use of the acylperoxide differently from what happens for the

acylperoxides known in the prior art.

The perfluorodiacylproxides of the invention are obtained

by synthesis of the corresponding perfluoroacylhalides in the

presence of H_2O_2 and NaOH. In particular, they can be prepared

by addition of perfluoroacylfluorides to a biphase system for-

med by a halogenated solvent and by an aqueous solution

containing H_2O_2 and an alkaline metal hydroxide, such as for

example NaOH, KOH. The halogenated solvent can be 1,1,2-tri-

chloro-1,2,2-trifluorethane, trichlorofluoromethane, perfluo-
roheptane, perfluoropolyethers. The fed amounts of perfluo-
racylfluoride range from 0.5 to 2 moles per mole of H_2O_2; the
amount of alkaline metal hydroxide is in the range 0.8-1.5
moles per mole of perfluoroacylfluoride. The system is
maintained under stirring in a temperature range from -15°C to
20°C, preferably from -5°C to +5°C. The organic phase
containing the reaction products in solution is recovered from
the aqueous phase by separation. A washing step with water of
the organic phase and subsequent anhydrification with sodium
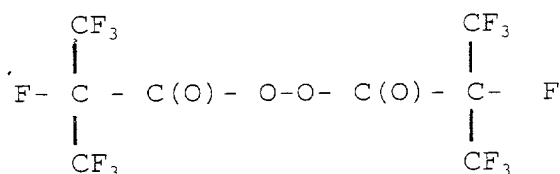sulphate follows.

A further object of the present invention is a polymeri-
zation process in solvent or in aqueous medium of one or more
fluorinated monomers wherein as polymerization initiators the
above perfluorodiacylperoxides are used.

As polymerization solvents, fluorinated solvents, prefe-
rably (per)fluoroalkanes or (per)fluoropolyethers are used.

As said the compounds of the invention can be used in a
wide temperature range depending on the polymerization type.
This is possible since the perfluorodiacylperoxides of the
invention decompose in a surprisingly wide temperature range.
For example, in the preparation of vinylidene fluoride (VDF)-
based polymers it is preferable to use low polymrization
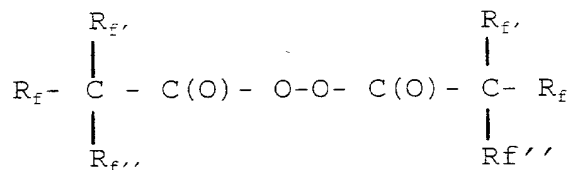temperatures (0°-10°C). Viceversa, in the case of copolymers

having a high content of not very reactive mono- mers, as in

the case of copolymers of 2,2,3-trifluoro-4-tri-fluoromethoxy-

1,3-dioxole (TTD), it is preferable to carry out the

polymerization at higher temperatures (higher than 50°C).

In particular for the polymerization reactions at tempe-

ratures of the order of 50°-80°C, the compounds of structure

(C) or the compound of structure (A) having the formula:

$$\begin{array}{ccccccc} & CF_3 & & & & CF_3 & \\ & | & & & & | & \\ F- & C & - C(O)- & O-O- & C(O)- & C- & F \\ & | & & & & | & \\ & CF_3 & & & & CF_3 & \end{array}$$

are preferably used.

For the polymerization ractions at low temperature, of

the order of -20° - +25°C, the compounds of structure (A) of

formula:

$$\begin{array}{ccccccc} & R_{f'} & & & & R_{f'} & \\ & | & & & & | & \\ R_f- & C & - C(O)- & O-O- & C(O)- & C- & R_f \\ & | & & & & | & \\ & R_{f''} & & & & Rf'' & \end{array}$$

are preferably used, wherein when R_f is -CF_3, $R_{f'}$ and $R_{f''}$ are

C_1-C_3 linear or branched perfluorooxyalkyl groups. Said acyl-

peroxides of group (A) can furthermore be used as polymeri-

zation initiators in solvent at a temperature lower than

0°C.

As fluorinated monomers polymerizable in the presence of

the perfluorodiacylperoxides of the invention, we can mention:

- C_2-C_8 perfluoroolefins, such as tetrafluoroethylene (TFE), hexafluoropropene (HFP);

- C_2-C_8 hydrogenated fluoroolefins, such as vinyl fluoride (VF), vinylidene fluoride (VDF), trifluoroethylene, CH_2=CH-R_f perfluoroalkylethylene, wherein R_f is a $C.$-C_6 perfluoroalkyl, hexafluoroisobutene;

- C_2-C_8 chloro-fluorolefins, such as chlorotrifluoroethylene (CTFE);

- CF_2=$CFOR_f$ (per)fluoroalkylvinylethers (PAVE), wherein R_f is a C_1-C_6 (per)fluoroalkyl, for example CF_3, C_2F_5, C_3F_7;

- CF_2=CFOX (per)fluoro-oxyalkylvinylethers, wherein X is: a C_1-C_{12} alkyl, or a $C.$-C_{12} oxyalkyl, or a C_1-C_{12} (per)flu-orooxyalkyl having one or more ether groups, for example perfluoro-2-propoxy-propyl;

- perfluorodioxoles, such as 2,2,4-trifluoro-5-trifluorome-thoxy-1,3-dioxole (TTD), 2,2-bis-trifluoromethyl-4,5-di-fluoro-dioxole (PPD);

- sulphonic monomers, such as for example CF_2=$CFOCF_2CF_2SO_2F$;

- fluorinated dienes as for example CF_2=$CFOCF_2CF_2CF$=CF_2, CF_2=$CFOCCl_2CF_2CF$=CF_2, CF_2=$CFOCF_2OCF$=CF_2, CF_2=$CFOCF_2OCCl$=CF_2, CF_2=$CFOC(CF_3)_2OCF$=CF_2.

The polymerization in aqueous medium can be carried out in suspension, in emulsion or in microemulsion in the presence
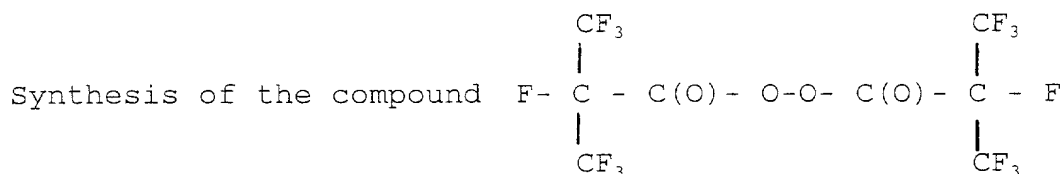
of the perfluorodiacylperoxides of the invention acting as initiators. The initiator feeding procedures can be in a continuous way or by a single addition at the starting of the polymerization. The amount of perfluorodiacylperoxide initiator is in the range 0.0001%-5% by moles with respect to the amount of the fed monomers.

The polymerization temperature can be in the range from -20°C to 80°C at pressures comprised between 2 and 50 bar.

In the case of polymerization in aqueous emulsion, the presence of a surfactant is necessary, the fluorinated surfactants such as perfluorooctanoate or mixtures of ammonium, potassium or sodium perfluorooctanoate, perfluorononanoate, perfluorodecanoate are particularly preferred. It is particularly suitable to carry out the polymerization in aqueous phase in the presence of perfluoropolyethers as surfactants. Said perfluoropolyethers can be added to the reaction medium under the form of microemulsion, as described in USP 4,864,006.

The present invention will now be better illustrated by the following embodiment Examples, which have a merely indicative purpose but not limitative of the scope of the inventiuon.

EXAMPLES

EXAMPLE 1

Synthesis of the compound

$$F-\underset{\underset{CF_3}{|}}{\overset{\overset{CF_3}{|}}{C}}-C(O)-O-O-C(O)-\underset{\underset{CF_3}{|}}{\overset{\overset{CF_3}{|}}{C}}-F$$

48.7 mmoles of NaOH (1.95 g) which are dissolved in 15 ml of bistilled water are introduced in a four-necked flask equipped with mechanical stirrer, solid CO_2 condenser, thermometer and dropping funnel. 50 ml of CCl_2FCClF_2 solvent are added and then the temperature of the system is lowered by a cold bath to about 0°C. 4.6 ml of H_2O_2 at 57.5% (corresponding to 94 mmoles of H_2O_2) are introduced and then, by the dropping funnel, 47 mmoles of $(CF_3)_2CFCOF$ (10.2 g) are introduced. The system temperature passes from 0°C to 8°C; the exothermic value of the reaction is controlled by the cold bath, maintaining the temperature at about 2°C. After 10 minutes the flask content is transferred into a separatory funnel and the organic phase is washed with distilled water until a neutral pH, then it is anhydrified with anhydrous Na_2SO_4. The peroxide concentration in CCl_2FCClF_2 is determined by iodometric titration. The reaction yield is 70%.

Characterization of the compound $[(CF_3)_2CFCOO]_2$

NMR^{19}F spectrum (with respect to $CFCl_3=0$)

−184 ppm 1F; −75 ppm 6F

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IR spectrum main bands (cm-1);

intensity: (w) = weak; (m) = mean; (s) = strong; (vs) = very strong:

1853 (m), 1824 (m), 1309 (m), 1264 (s)

Mass spectrum (E.I electronic impact), main peaks and respective intensities:

319 (3), 281 (3), 231 (5), 181 (5), 131 (5), 69 (100)

Decomposition constants

The thermal decomposition constants K_d (sec^{-1}) of the perfluorodiacylperoxide of the invention are determined under anhydrous conditions at different temperatures, equal to 60°C, 70°C, 80°C.

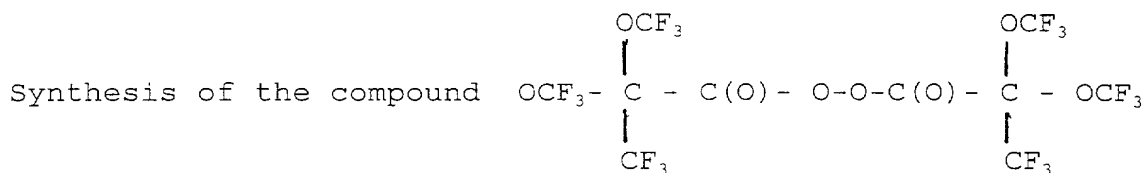By using as solvent CCl_2FCClF_2 and a peroxide concentration equal to 6% by weight, the following results are obtained:

$K_d = 4.4\cdot10^{-5}$ (60°C); $16.2\cdot10^{-5}$ (70°C); $57.8\cdot10^{-5}$ (80°C).

Subsequently it is seen that the decomposition constants, determined at the same temperatures of 60°C, 70°C and 80°C, introducing 0.5 ml of H_2O per ml of peroxidic solution under magnetic stirring and titrating the organic layer, do not undergo significant variations with respect to the respective above reported thermal decomposition constants.

Besides the pH of the aqueous phase, during the described hydrolytic decomposition, remains unchanged and the only de-

composition products are: CO_2 and $(CF_3)_2CFCF(CF_3)_2$.

EXAMPLE 2

Synthesis of the compound
$$OCF_3-\underset{\underset{CF_3}{|}}{\overset{\overset{OCF_3}{|}}{C}}-C(O)-O-O-C(O)-\underset{\underset{CF_3}{|}}{\overset{\overset{OCF_3}{|}}{C}}-OCF_3$$

The synthesis procedure is equal to that used in Example 1 with the following quantitative modifications:

26 mmoles of $(CF_3)(CF_3O)_2CCOF$ (7.8 g), 35 mmoles of NaOH (1.39 g), 15 ml of bidistilled water, 3.0 ml of H_2O_2 at 57.5% (62 mmoles) and 50 ml of CCl_2FCClF_2 solvent.

It is let react for 90 min, following the acylfluoride disappearance by IR analysis. The reaction yield is 46%.

Characterization of the compound $[(CF_3)(CF_3O)_2CCOO]_2$

NMR^{19}F spectrum (with respect to $CFCl_3 = 0$):

-59 ppm 6F, -82 ppm 3F

IR spectrum main bands (cm-1);

intensity: (w) = weak; (m) = mean; (s) = strong; (vs) = very strong:

1854 (m), 1828 (m), 1287 (s), 1254 (s)

Mass spectrum (E.I electronic impact), main peaks and respective intensities:

263 (6), 251 (3), 135 (2), 97 (4), 69 (100)

Decomposition constants

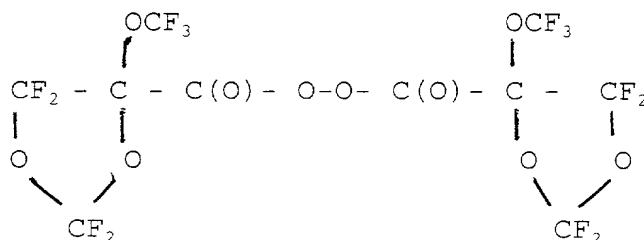Decomposition constants K_d (sec^{-1}) and respective tempera-

tures determined under anhydrous conditions (CCl_2FCClF_2 as solvent):

K_d = 1.8· 10^{-5} (5°C); 7.6· 10^{-5} (15°C); 46.2· 10^{-5} (25°C).

The decomposition constant in the presence of water is determined at the temperature of 15°C, maintaining under magnetic stirring 8 ml of peroxidic solution and 8 ml of water and titrating the organic layer. No significant variation is noticed with respect to the respective thermal decomposition constant in absence of water.

EXAMPLE 3

Synthesis of the compound

$$CF_2 - \underset{\displaystyle O}{\overset{\displaystyle OCF_3}{\underset{|}{\overset{|}{C}}}} - C(O) - O-O- C(O) - \underset{\displaystyle O}{\overset{\displaystyle OCF_3}{\underset{|}{\overset{|}{C}}}} - CF_2$$

The synthesis procedure is equal to that used in Example 1 with the following quantitative modifications:

23 mmoles of acylfluoride (6.4 g), 25 mmoles of NaOH (0.99 g), 16 ml of bidistilled water, 2.1 ml of H_2O_2 at 57.5% (43 mmoles) and 45 ml of CCl_2FCClF_2 solvent. The reaction yield is 56%.

Characterization of the compound

$NMR^{19}F$ spectrum (with respect to $CFCl_3$ = 0):

-55 ppm 1F, -56 ppm 3F, -59 ppm 1F, -75 ppm 1F, -90 ppm 1F

IR spectrum main bands (cm-1);

intensity: (w) = weak; (m) = mean; (s) = strong; (vs) = very strong:

1857 (m), 1828 (m), 1349 (m), 1236 (s)

Mass spectrum (E.I electronic impact), main peaks and respective intensities:

229 (42), 163 (21), 135 (7), 116 (3), 97 (30), 78 (4), 69 (100), 50 (6)

Decomposition constants

Decomposition constants K_d (sec^{-1}) and respective temperatures determined under anhydrous conditions (CCl_2FCClF_2 as solvent):

K_d = 3.1· 10^{-5} (20°C); 11.7· 10^{-5} (30°C); 50.2· 10^{-5} (40°C).

The decomposition constant in the presence of water is determined at the temperature of 30°C, maintaining under magnetic stirring 8 ml of peroxidic solution and 8 ml of water and titrating the organic layer. No significant variation is noticed with respect to the respective thermal decomposition constant in absence of water.

EXAMPLE 4

The perfluorodiacylperoxide $[(CF_3)_2CFCOO]_2$ obtained in Example 1 is used as polymerization initiator in suspension for the preparation of the vinylidene fluoride (VDF) homopolymer.

0.12 mmoles of $[(CF_3)_2CFCOO]_2$ dissolved in CCl_2FCClF_2 (1.2

ml) and 20 ml of bidistilled water are introduced into a 50 ml steel reactor, equipped with magnetic stirrer. The so charged reactor is subjected to three cycles reaching the room temperature, condensation in liquid nitrogen, and evacuation at the pressure of 10^{-3} mbar to remove oxygen traces. At the end of these steps 22 atm of VDF are introduced into the reactor and then the system is maintained, under magnetic stirring, at the temperature of 57°C.

When the pressure in the autoclave decreases to 15 atm one provides for the monomer restoration up to the value of 20 atm. After 48 hours the unreacted monomer is removed, obtaining 3.3 g of homopolymer equivalent to a 90% yield.

EXAMPLE 5 (comparative)

One proceeds as in Example 4, but using the peroxide having a linear structure $[CF_3CF_2CF_2OCF(CF_3)CF_2OCF(CF_3)COO]_2$ instead of the perfluoroacylperoxide $[(CF_3)_2CFCOO]_2$ of the invention. While maintaining all the other reaction parameters equal, 0.5 g of VDF homopolymer, equivalent to a yield of 16%, are obtained.

EXAMPLE 6

The perfluorodiacylperoxide of formula $[(CF_3O)_2(CF_3)CCOO]_2$ obtained in Example 2 is used as polymerization initiator in solution for the preparation of the vinylidene fluoride (VDF) homopolymer.

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0.15 mmoles of $[(CF_3O)_2(CF_3)CCOO]_2$ dissolved in CCl_2FCClF_2 (1.4 ml) and 8.6 ml of perfluoropolyether solvent GALDEN® LS-155 are introduced into a 50 ml steel reactor, equipped with magnetic stirrer. The so charged reactor is subjected to three cycles reaching the room temperature, condensation in liquid nitrogen, and evacuation at the pressure of 10^{-3} mbar to remove oxygen traces. At the end of these steps the reactor is heated to 5°C and then gaseous VDF is introduced until the monomer dissolved in the solvents is in equilibrium with a pressure of 15 atm of gaseous monomer. The system is maintained, under magnetic stirring, at the temperature of 5°C for one hour, at the end of which the unreacted monomer is outgassed obtaining, after thermal treatment at 120°C under vacuum for 5 hours, 3.3 g of VDF homopolymer equivalent to a 65% yield.

EXAMPLE 7 (comparative)

One proceeds as in Example 6, but using the peroxide having a linear structure $[CF_3CF_2CF_2OCF(CF_3)CF_2OCF(CF_3)COO]_2$ instead of the peroxide $[(CF_3O)_2(CF3)CCOO]_2$ of the invention. While maintaining all the other reaction parameters equal, 1.5 g of VDF homopolymer, equivalent to a 29% yield, are obtained.

EXAMPLE 8

The peroxide $[(CF_3)_2CFCOO]_2$ obtained in Example 1 is used as polymerization initiator in emulsion for preparing the VDF homopolymer.

In this and in all the subsequent Examples of polymerization in emulsion, with "emulsifier" a microemulsion salified with sodium is meant, prepared according to USP 4,846,006 in the name of the Applicant.

0.106 g of emulsifier and 10.030 g of bidistilled water and then, after a short stirring, 1 ml of a peroxide solution in CCl_2FCClF_2 solvent containing 0.15 mmoles of $[(CF_3)_2CFCOO]_2$ are introduced into a 50 ml steel reactor, equipped with magnetic stirrer. The so charged reactor is subjected to two cycles reaching the room temperature, condensation in liquid nitrogen, and evacuation at the pressure of 10^{-3} mbar to remove oxygen traces. At the end of these steps 25 atm of VDF are introduced into the reactor and then the system is maintained, under magnetic stirring, at the temperature of 57°C. After 6 hours the unreacted VDF is outgassed, obtaining 2.1 g of homopolymer equivalent to a 58% yield.

EXAMPLE 9 (comparative)

The peroxide having linear structure $[CF_3CF_2CF_2COO]_2$ is used as polymerization initiator in emulsion for preparing the VDF homopolymer.

0.104 g of emulsifier and 10.431 g of bidistilled water and then, after a short stirring, 1 ml of a peroxide solution in CCl_2FCClF_2 solvent containing 0.15 mmoles of $[CF_3CF_2CF_2COO]_2$ are introduced into a 50 ml steel reactor, equipped with

magnetic stirrer. The so charged reactor is subjected to two

cycles reaching the room temperature, condensation in liquid

nitrogen, and evacuation at the pressure of 10^{-3} mbar to remove

oxygen traces. At the end of these steps 25 atm of VDF are

introduced into the reactor and then the system is maintained,

under magnetic stirring, at the temperature of 57°C. After 6

hours the unreacted VDF is outgassed, obtaining 0.5 g of homo-

polymer equivalent to a 14% yield.

EXAMPLE 10

The peroxide $[(CF_3O)_2(CF_3)CCOO]_2$ obtained in Example 3

is used as polymerization initiator in emulsion for preparing

the vinylidene fluoride homopolymer.

0.108 g of emulsifier and 10.042 g of bidistilled water

and then, after a short stirring, 1 ml of a peroxide solution

in CCl_2FCClF_2 containing 0.15 mmoles of $[(CF_3)(CF_3O)_2CCOO]_2$ are

introduced into a 50 ml steel reactor, equipped with magnetic

stirrer. The so charged reactor is subjected to two cycles

reaching the room temperature, condensation in liquid ni-

trogen, and evacuation at the pressure of 10^{-3} mbar to remove

oxygen traces. At the end of these steps 25 atm of VDF are

introduced into the reactor and then the system is maintained,

under magnetic stirring, at the temperature of 6°C. After 6

hours the unreacted VDF is outgassed, obtaining 2.8 g of homo-

polymer equivalent to a 78% yield.

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EXAMPLE 11

In a 500 cc Hastelloy autoclave equipped with stirrer working at 800 rpm, after the vacuum has been made, 300 cc of water, 5.3 g per litre of water of an ammonium salified microemulsion prepared according to USP 4,864,006 in the name of the Applicant, are introduced in sequence.

Then the autoclave is heated up to 60°C, when it has reached the temperature 65 g of 2,2,3-trifluoro-4-trifluoro-methoxy-1,3-dioxole (TTD) are introduced, then tetrafluoroe-thylene (TFE) is introduced until reaching 9 absolute bar of pressure. 0.6 g of the peroxide $[(CF_3)_2CFCOO]_2$ obtained in Example 1 dissolved in GALDEN® D80 are fed, the solution has a concentration of 0.1 g/cc.

After the reaction starting the pressure is maintained constant by feeding TTD and TFE in a ratio by weight TTD/TFE equal to 18.9. After 220 minutes the reaction is stopped and the latex is discharged.

The product is coagulated with HNO_3, the polymer is dried in a stove at 120°C for 18 hours and then treated at 230°C for 2 hours.
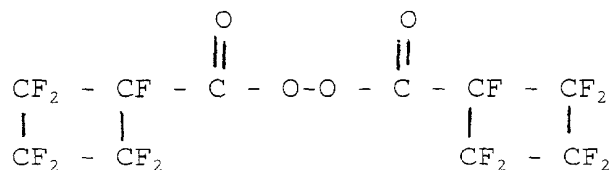
Charaterization of the TTD/TFE copolymer

The molar composition of the monomers incorporated into the polymer is: 48% TTD, 52% TFE. All the polymer chain end groups are perfluorinated.

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By the infrared spectrum in the absorption zone 1780-1880 it is found the substantial absence of carbonyl and carboxyl groups.

The polymer is amorphous and shows a sole Tg of 106.4°C at the DSC analysis.

EXAMPLE 12

Synthesis of the compound $(c\text{-}C_4F_7COO)_2$

$$CF_2 - CF - \overset{\overset{\displaystyle O}{\|}}{C} - O\text{-}O - \overset{\overset{\displaystyle O}{\|}}{C} - CF - CF_2$$
$$CF_2 - CF_2 \qquad\qquad\qquad CF_2 - CF_2$$

The synthesis procedure is equal to that used in Example 1 with the following quantitative modifications:

30 mmol of $c\text{-}C_4F_7COF$ (6.8 g), 33 mmol of NaOH (1.32 g), 10 ml of bidistilled water, 6.0 ml of H_2O_2 at 30% (60 mmol) and 30 ml of CCl_2FCClF_2 solvent. It is let react for 10 minutes, following the acylfluoride disappearance by IR analysis. The reaction yield is 55%.

Characterization of the compound $(c\text{-}C_4F_7COO)_2$

^{19}F NMR spectrum (with respect to $CFCl_3 = 0$):

-126 ppm 2F, -130 ppm 2F, -131 ppm 2F, -188 ppm 1F

IR spectrum main bands (cm^{-1}):

intensity: (w) = weak; (m) = medium; (s) = strong; (vs) = very strong:

1843 (m), 1817 (m), 1289 (s), 1232 (s)

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Mass spectrum (E.I. Electronic Impact), main peaks and respective intensities:

293 (25), 262 (12), 243 (20), 193 (29), 162 (47), 100 (100), 69 (37).

Decomposition constants

Decomposition constants K_d (sec^{-1}) and respective temperatures determined under anhydrous conditions (CCl_2FCClF_2 as solvent):

K_d = 11 x 10^{-5} (70°C); 36 x 10^{-5} (80°C).

EXAMPLE 13

The perfluorodiacylperoxide $[(CF_3)_2CFCOO]_2$ obtained in Example 1 is used as polymerization initiator of the TTD (2,2,3-trifluoro-4-trifluorometoxi-1,3-dioxol).

9.3 g (44 mmol) of TTD and 0.044 mmol of $[(CF_3)_2CFCOO]_2$ dissolved in CCl_2FCClF_2 are introduced into a 50 ml polymer-isation glass reactor, equipped with magnetic stirrer. The so charged reactor is subjected to three cycles reaching thr room temperature, condensation in liquid nitrogen and evacuation at the pressure of 10^{-3} mbar to remove oxygen traces. At the end of these steps the system is maintained, under magnetic stirring, at the temperature of 57°C for 24 hours; then the same quantity of initiator is introduced in the reactor, and the system is let react for 24 hours a second time; the same operations are repeated the third day. After three days at

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57°C, the unreacted monomer is removed, keeping the reactor at the temperature of 130°C and at the pressure of 10^{-3} mbar for one hour. 3,6 g of homopolymer are obtained, equivalent to a 39% yield.

Characterization of TTD hmopolymer

DSC: T_g = 176,1°C

TGA: -1% 332°C, -2% 356°C, -10% 399°C, -50% 432°C

EXAMPLE 14 (comparative)

One proceeds as in Example 13, but using the peroxide $[CF_3CF_2C(O)O]_2$ instead of the perfluorodiacylperoxide $[(CF_3)_2CFCOO]_2$ of the invention. While maintaining all other reaction parameters equal, except the reaction temperature (which is 27°C), 0,3 g of TTD homopolymer, equivalent to a yield of 5%, are obtained.